## CLAIMS:

- 1. A method of preparing derivatized peptides to enhance mass spectral analysis of peptide containing compositions, said method comprising the steps of: providing a composition comprising a peptide; and labeling N-termini of the peptide with a compound selected from the group consisting of an acetamidine group and a propionamidine group.
- 2. The method of claim 1 further comprising the step of blocking lysine residues of the peptide or protein with guanidination.
- 3. The method of claim 2, wherein said guanidination is performed with S-methylisothiourea or O-methylisourea..
- 4. The method of claim 1 or 3, wherein the N-termini are labeled with an acetamidine group utilizing S-methyl thioacetimidate.
- 5. The method of claim 1 or 3, wherein the N-termini are labeled with a propionamidine group utilizing S-methyl thiopropionimidate.
- 6. The method of claim 1 or 2 further comprising the step of dividing said peptide composition into a first and second pool of peptides; and wherein said labeling step comprises

labeling the N-termini of the peptides of said first pool of peptides with an acetamidine group; and

labeling the N-termini of the peptides of said second pool of peptides with a propionamidine group.

7. The method of claim 1 or 2 further comprising the step of dividing said peptide composition into a first and second pool of peptides; and wherein said labeling step comprises

labeling the N-termini of the peptides of said first pool of peptides with an amidine group; and

labeling the N-termini of the peptides of said second pool of peptides with an amidine group that comprises an isotopic substituted group, wherein the amidine group and the labeled amidine group have different molecular weights.

- The method of claim 7 wherein the amidine group is selected from 8. the group consisting of an acetamidine group, a propionamidine group, a butyramidine group and a pentylamidine group.
- 9. The method of claim 8 wherein the labeled amidine group comprises an amidine wherein a H group is substituted with deuterium, or a C12 group is substituted with  $C^{14}$ .
- The method of claim 9 wherein the mass spectral analysis includes 10. tandem MS/MS.
- The method of claim 10, wherein said guanidination is performed 11. with S-methylisothiourea
- 12. The method of claim 10 wherein the N-termini of the peptides of said first pool of peptides are labeled utilizing S-methyl thioacetimidate, and the Ntermini of the peptides of said second pool of peptides are labeled utilizing S-methyl thiopropionimidate.
- 13. A set of modified tryptic peptides, said set comprising a first pool of peptides wherein N-termini of said first pooled peptides are labeled with an acetamidine group; and a second pool of peptides wherein N-termini of said second pooled peptides are labeled with a propionamidine group.
- 14. The set of peptides of claim 13 wherein the peptides of the first and second pools are identical except for the N-terminal labels.

- 15. The set of peptides of claim 14 wherein the lysine residues of the peptides of the first and second pools are converted to homoarginines.
- 16. The set of peptides of claims 14 or 15 wherein the N-termini of the peptides of said first pool of peptides are labeled utilizing S-methyl thioacetimidate, and the N-termini of the peptides of said second pool of peptides are labeled utilizing S-methyl thiopropionimidate.